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(54) Title: IMPROVEMENTS TO POLYMERISATION PROCESSES

(57) Abstract: A polymerisation process comprises an initiation step, taking place between at least one initiator compound and at least one species of monomer, a propagation step and a termination step, at least the propagation step being carried out within a liquefied gas continuous phase. The liquefied gas continuous phase may comprise a C₁ to C₄ hydrofluorocarbon, such as 1,1,1,2-tetrafluoroethane. The use of one or more polymers, at least one of which contains a basic nitrogen-containing moiety, as a cationic gelling agent is also provided.

Improvements to Polymerisation Processes

This invention relates to processes for the production of polymers.

The simplest means for the preparation of a polymer is to directly react a monomer or mixture of monomers with one of a range of initiators in a container. The polymers so formed may be solids which take up the shape of the container and can thereafter be harvested in the form of a block or sheet which is then available for melting, extrusion, granulation or other treatment to render the polymer into a physical form suitable for further use.

A second technique which may represent an improvement upon this simple procedure is to employ a third material in the form of a liquid which has the ability to function as a suspending agent in which the polymer, once a given degree of polymerisation is reached, is not soluble. This liquid may be referred to as the "continuous phase".

The monomer may be soluble in the continuous phase, in which case polymer particles can (upon monomer being brought into reactive contact with an initiator system) be built into a preferred particle size by adjusting the concentration of monomer in solution in the continuous phase.

If the monomer is not soluble in the continuous phase, it may be suspended in it in the form of droplets which may then be formed into discrete particles of the polymer, upon being brought into reactive contact with a suitable initiator system.

If the monomer is not soluble in the continuous phase itself, but is soluble in another solvent which is itself, also, not soluble in the continuous phase, a suspension of droplets of the monomer solution (the monomer being in solution in, for example, water) may be caused to polymerise when the droplets of solution are brought into reactive contact with an initiator system.

The ability to dissolve monomer or suspend monomer particles or droplets, or suspend droplets of a solution of monomer in another solvent, in such a fluid continuous phase, provides the chemist with a means of stirring the mixture of monomer in the suspending fluid. This may be helpful in maintaining separate from each other the particles of polymer being formed during the polymerisation reaction.

This provides means for generating the polymer in the form of suspended droplets or "beads" or even (if particles of polymer are small enough) as a stable emulsion, suspended in the continuous phase.

The use of this technology and in particular the correct choice of continuous phase allows the chemist not only to produce particles or beads of the final product of closely defined mesh sizes, but may also simplify and extend the chemist's ability to control the rate at which the polymerisation takes place.

If, for example, into the continuous phase is carefully fed monomer at a first very slow rate and initiator at another very slow rate continuously, over a long period, it is possible to provide polymers of an extremely discrete range of molecular weights. The spread of molecular weights of a sample of polymer is known as its "polydispersity". In many applications it is frequently desirable to employ polymers with well defined, reproducible and low degrees of polydispersity, in which all or a substantial majority of the polymer molecules have the same or similar molecular weights (chain length).

Factors influencing the polydispersity of a polymer are not only the ratio of monomer to initiator, but also the rate at which these two materials are brought into contact.

The continuous phase, being a liquid and usually present in excess of either monomer or initiator, is easily able to absorb, from the polymer droplets, any heat which may be given off during the process of polymerisation. It is well known that most polymerisations induced by free radical systems employing "unsaturated" monomers (i.e. molecules having at least one carbon-carbon multiple bond) give off substantial amounts of heat. This is

known as the "exotherm" of the reaction. The exotherm is a constant characteristic of the polymerisation of any specified monomer or mixed co-polymer system.

For example, in the case of acrylamide polymerisation and acrylamide/acrylic acid co-polymer systems in aqueous solution, the exotherm (which can cause a very substantial rise in temperature of the polymerisation system) during polymerisation is of the order of 71 kJ (17 K Cals) per mole of monomer.

This rise in temperature is frequently undesirable, causing a hold up in production whilst the heat is dissipated. Perhaps more importantly, the temperature rise may cause thermal damage to the final product and a reduction in its ultimate quality. This damage may be in terms of an increased tendency of the polymer molecules to "cross-link" thereby reducing their final solubility in water, greatly reducing their utility and quality. Alternatively or additionally, it may take the form of promoting hydrolysis of, for example, an acrylamide to an acrylic acid, thereby changing the ionisation character of the final product (from non-ionic to anionic or from cationic to non-ionic).

To minimise these effects, the continuous phase may be employed as a fluid heat exchange medium, particularly if it is stirred. It can be easily and rapidly cooled or maintained within a defined temperature range, thereby eliminating the effects of these damaging exotherms. The more dilute the mixture of monomer(s) in the continuous phase, the lower will be any change in temperature during polymerisation. Thermal degradation will therefore be proportionately reduced.

A further advantage of forming polymers as droplets, beads, a suspension or an emulsion in a continuous phase, especially if the monomers are soluble in the continuous phase and the polymer insoluble, derives from the ability to quickly harvest the polymer, simply by filtration of the polymer/continuous phase mixture. Unreacted monomer may thereby be removed from the vicinity of the polymer immediately upon, or shortly after, its formation. This has two advantageous effects. The first is to curtail further secondary polymerisation of monomer upon previously formed polymer particles and the second is to rid the harvested polymer of unreacted (free) monomer. The removal of unreacted monomer is

desirable as many monomers are highly toxic by ingestion or inhalation or are even flammable. Accordingly, the presence of free monomers in the final polymer is highly undesirable and producers of polymer products (particularly those intended for ingestion by humans) must go to great pains to eliminate or substantially rid their products of any trace of toxic free monomers. The filtered polymer product must usually also be rendered substantially free of solvent residues before its use or further processing.

It is known to carry out polymerisation of methyl methacrylate in supercritical carbon dioxide (*Science* 265, 321 (1994)). The capital and running expense of such a process, however, in terms of the use of high pressurisation facilities, tends to limit its general applicability.

It is therefore an object of the present invention to provide polymerisation processes which have advantages over the prior art in at least one of the above respects.

Accordingly, one aspect of the present invention provides a polymerisation process comprising an initiation step, taking place between at least one initiator compound and at least one species of monomer, a propagation step and a termination step, at least the propagation step being carried out within a liquefied gas continuous phase.

The term 'liquefied gas' as used herein means a compound which is normally gaseous at room temperature and pressure and which has been condensed to a sub-critical liquid by application of pressure and/or reduction of temperature. The liquefied gas continuous phase may include one or more co-solvents, miscible with the liquefied gas, and which may or may not be liquefied gases themselves. Co-solvents, when used, are preferably present in a proportion appropriate to form an azeotropic continuous phase, i.e. a constant boiling mixture which does not change in composition upon distillation and recondensation.

Advantageously, the initiation and/or termination steps are also carried out within the liquefied gas continuous phase.

The expression 'carried out within the liquefied gas continuous phase' includes the situation where the liquefied gas is a dispersant continuous phase for an additional immiscible solvent in which one or more of the reactant species are dissolved, as well as the situation where the liquefied gas is a solvent for all the reactant species.

It is preferred that all steps of the polymerisation process which involve the use of the liquefied gas continuous phase are carried out in a sealed pressure container. Such a pressure container may be sealed by means of an aerosol-type valve or a ball valve. The container is preferably capable of withstanding an internal pressure of 1000 kPa (10 bar), more preferably 2000 kPa (20 bar).

The initiator compound is preferably of the type which becomes reactive to the monomer on exposure to electromagnetic, particularly ultraviolet, radiation, although other types, such as redox couples, may be used where appropriate. An example of a suitable redox couple initiator comprises ferrous ions (possibly in the form of a solution of ferrous ammonium sulphate) and ammonium persulphate (or other persulphates or peroxides). A preferred type of initiator is one which causes the formation of monomer free radicals. The initiator compound may comprise an activated form, such as a free radical, of a monomer itself.

The initiator compound and the monomer may both be dissolved in the liquefied gas continuous phase. Alternatively, one species may be present in the liquefied gas continuous phase and another species may be present in an additional solvent phase immiscible or partially-immiscible with the liquefied gas continuous phase. This additional solvent phase may comprise water. A surfactant may be added to one or more of the liquefied gas and additional solvent phases so as to aid in the formation of a dispersion of one phase in the other and/or so as to aid in the dispersion of polymer particles in the solvent as they are forming.

It is also possible to have both the monomer and initiator compounds present in the additional solvent phase during the initiation step. The mixture is then dispersed in the liquefied gas phase for the propagation step. This mode of operation of the process is less

preferred because of the need to add liquefied gas phase extremely quickly after mixture of the initiator and monomer.

The termination step may comprise the addition of a specific termination compound, such as a chain transfer reagent or chain terminator, or may be accomplished by the exhaustion of one of the monomer species or of the initiator compound. Examples of chain transfer reagents include thioglycolic acid, iso-propanol and nitric oxide.

In preferred embodiments of the invention, the liquefied gas is selected from the group comprising C₁ to C₄ hydrofluorocarbons, C₁ to C₄ straight chain, branched or cyclo-alkanes selected from those which are gaseous at room temperature and pressure, C₁ to C₄ perfluorocarbons, C₁ to C₄ iodofluorocarbons such as those listed in EP0687287, dimethyl ether, hydrogen sulphide, sulphur dioxide, chlorine, nitrous oxide, nitrogen dioxide, carbon disulphide, ammonia, carbon monoxide, carbon dioxide and argon.

Of the preferred liquefied gases, more preferred compounds include: hydrofluoromethanes, such as fluoromethane, difluoromethane, and trifluoromethane; hydrofluoroethanes, such as pentafluoroethane, 1,1,1-trifluoroethane, 1,1,1,2-tetrafluoroethane and 1,1,2,2-tetrafluoroethane; hydrofluoropropanes, such as 1,1,1,2,3,3-hexafluoropropane, 1,1,1,2,2,3-hexafluoropropane and 1,1,1,3,3,3-hexafluoropropane; perfluoropropane; and iodotrifluoromethane.

It is preferred that, if a hydrofluorocarbon is used, it has a boiling point of 15°C or below, more preferably in the range -85 to 0°C.

A particularly preferred liquefied gas compound is 1,1,1,2-tetrafluoroethane (also known as HFC134a).

Suitable co-solvents, other than liquefied gases, which may be combined with the liquefied gas continuous phase, include straight chain, branched or cyclo-alkanes selected from those which are liquid at room temperature and pressure, and diethyl ether.

The careful selection of continuous phase can provide the manufacturer with a simple means of further reducing the free monomer levels of his products by washing of the filter cake (of polymer granules) with further quantities of continuous phase. It is even possible that the continuous phase (still containing free monomer in solution) may be re-useable in a batch-wise or even continuous polymerisation process. In this case continuous phase filtrate and washings might be combined to form further monomer rich continuous phase for the next batch of polymer production, it only requiring the addition of more monomer and/or initiator to re-start the process.

This procedure provides the manufacturer with a harmless means of controlling the degree of polymerisation, by using the careful control of initiator as a means of determining the end-point of polymer formation. The physical form of the polymer can hence be controlled by starvation of initiator even in the presence of a substantial surplus of monomer. At present, quite the reverse applies, in so far as most manufacturers need to employ vast excesses of initiator in the hope of reducing the monomer concentration, the reduction of monomer concentration thereby limiting the rate of the process.

Preferred monomers for use in the present process include those having at least one carbon to carbon multiple bond. Particularly preferred monomers comprise vinyl or acrylate groups. The most preferred monomers have vinyl or acrylate groups and are substituted with basic nitrogen-containing moieties, such as amino. The quaternary ammonium salts of such monomers may also be used.

The process of the present invention has the considerable advantage that, following termination of the polymerisation reaction, the continuous phase can be quickly and efficiently removed from the product simply by releasing the pressure (if a sealed container is used) or by raising the temperature, or both. This simplicity of operation is accomplished without the requirement for high-pressure plant such as is required for supercritical fluid operations.

The ready removal of the continuous phase also provides a means by which unreacted monomer, either from a harvesting / filtration operation or from washing of the product

with continuous phase, can be recovered. The evaporated continuous phase can also be recovered by condensation and this enables it to be reused.

The invention is capable of being used with amino-containing monomers or their quaternary ammonium salts. Such monomers produce cationic polymers when subjected to the process of the invention or any similar process not using a liquefied gas continuous phase. These cationic polymers, or their quaternary ammonium salts, can be used as cationic gelling agents which show a marked increase in the viscosity of their aqueous solutions at basic pH.

Accordingly, a further aspect of the invention provides the use of one or more polymers, at least one of which contains a basic nitrogen-containing moiety, as a cationic gelling agent.

Preferred polymers for use in this aspect of the invention include those formed from monomers containing basic nitrogen-containing-moieties and acrylate or vinyl groups, or quaternary ammonium salts of such monomers. Examples of such monomers include dimethylaminopropylmethacrylamide (DMAPMA), dimethylaminopropylacrylamide (DMAPA), dimethylaminoethylmethacrylate (DMAEMA), *N*-vinylformamide (NVF), *N*-vinyl-2-pyrrolidinone (NVP) and their quaternary ammonium salts.

Preferably, the polymers are obtained by means of the polymerisation process of the present invention.

The invention will now be described in more detail by way of example only.

Compared to many other frequently used materials, a liquefied gas such as the hydro-fluorocarbon 1,1,1,2-tetra fluoroethane (HFC134a), provides an improved continuous phase in which to carry out bead, emulsion or suspension polymerisation reactions.

Its particular advantages are, for example,

1. it is chemically inert,
2. it is non-toxic and
3. it is not flammable.

Reactions in which HFC134a are carried out can be handled in low cost capital equipment, as it has a vapour pressure of only 500 kPa (5 BarG) at 20 degrees Celsius.

The viscosity of HFC134a is only 0.22 centipoise and hence suspensions of polymers in this solvent can be stirred very easily and the filtration to produce and wash the final filter cake is extremely simple and rapid.

The ability of HFC134a to act as a heat exchange medium is aided by its very low boiling point (-26 degrees Celsius). Control of reaction temperature can easily be achieved by controlling the rate of condensation of the vapour of the liquefied gas continuous phase, using a heat exchanger cooled with brine or glycol. The rate of such cooling may be automatically controlled by reference to the rise in the vapour pressure within the polymerisation vessel.

Many monomers dissolve in liquefied gases such as HFC134a and hence controlling the degree of polymerisation is very simply achieved by control of initiator input. Furthermore, free monomer can easily be washed out of the final polymer by washing of the suspension or filter cake with clean continuous phase. This can readily be achieved by using condensed, distilled continuous phase obtained using a robust soxhlet extraction system.

A valuable advantage of using HFC134a as a continuous phase derives from its low boiling point. It boils at -26 degrees Celsius (at atmospheric pressure) and thus polymers prepared using this material as continuous phase require little or no additional "drying" as the continuous phase evaporates essentially completely from the polymer at room temperature and atmospheric pressure leaving virtually no trace.

Rather than directly re-using monomer contained in solution in the filtrate (continuous phase) after polymerisation, it can be readily and easily recovered in the dry state by evaporation of the continuous phase. Condensation of the continuous phase vapours at each of the above stages enables it to be completely or substantially recovered, for recycling and re-use.

EXAMPLES

Example 1.

50 grams of an aqueous solution comprising 47.7 % w/w of acrylamide was introduced into a stirring glass reactor furnished with a means for sparging the contents with oxygen free nitrogen (OFN) and capable of withstanding 1000 kPa (10 BarG) of internal pressure and to which it was possible to introduce further liquid materials.

To this solution was added 50 mg of a solution of the surfactant Tetralon A. The pH of this mixture was adjusted to 6.0 by the incremental addition of 1 % w/w aqueous hydrochloric acid. A small quantity of aqueous sodium sulphite solution was also added.

A flow of nitrogen was commenced and the mixture was rendered substantially free of any oxygen it may have contained. The nitrogen was vented to atmosphere. The vessel was sealed with an "aerosol valve" system through which further liquid additions could be introduced. 250 grams of HFC134a was introduced into the reactor through the aerosol valve and stirring was commenced.

To the stirring mixture was added 0.3 ml of 70 % w/w stock solution of t-butyl hydroperoxide. After a few seconds, the temperature of the mixture (and the pressure inside the reactor) were seen to rise. Both rose to a maximum and after a further few minutes of observation, the temperature ceased to rise further and both the temperature and the pressure were seen to slowly decline.

After waiting for the temperature to decline to ambient and the pressure to fall back to 500 kPa (5 BarG) (the vapour pressure of HFC134a at this ambient temperature) the stirring was discontinued and the HFC134a was vented to a compressor, whereby it was condensed and collected for subsequent re-use.

The residue in the reactor proved to comprise a slurry of gelatinous spherical beads. These were dried in a small fluidised bed dryer and formed a free flowing white powder. This powder proved to be soluble in water and displayed the normal characteristics of a high molecular weight polyacrylamide solution, in that it formed a crystal clear, highly viscous, homogeneous solution.

Example 2.

50 kilograms of an aqueous solution of 50% acrylamide was de-oxygenated by sparging with OFN. The solution was introduced into a stainless steel pressure reactor, capable of withstanding 2000 kPa (20 BarG) pressure, which was equipped with a stirrer and cooling coils which were capable of being fed with glycol from a refrigerated reservoir at zero degrees Celsius. 150 kilograms of HFC134a was introduced into the reactor together with 20 grams of Tween 80. The mixture was stirred vigorously.

Two glass pressure vessels (Michael Miller HPLC glass columns (Supelco), capable of withstanding 1400 kPa (200 psiG)), each containing 100 ml of de-ionised water, were de-oxygenated by sparging with OFN. To one of these cylinders was added one gram of ammonium persulphate. To the other was added 1 gram of ferrous ammonium sulphate. The solution of ammonium persulphate was added to the stirred mixture in the extractor. After ten minutes, the solution of ferrous ammonium sulphate was added to the mixture.

Very quickly, a rise in temperature of the contents of the reactor and its internal pressure were observed and a flow of coolant was begun through the cooling coils. The cooling was monitored to ensure that the pressure in the reactor did not exceed 1000 kPa (10 BarG). This monitoring was maintained for 40 minutes.

The HFC134a was removed by coupling the reactor to the inlet of a compressor whereby it was re-condensed and collected for re-use.

The distillation process caused a rapid reduction in the pressure and temperature of the contents of the reactor and heating was supplied to the stirred contents to hasten evaporation of the HFC134a.

When all the HFC134a had been recovered, a slurry of gelatinous beads of polyacrylamide was left in the reactor. This slurry was dried to 88 % solids (12 % water) to a fine free flowing powder consistency. The particles were seen to be of remarkably uniform size and were spherical. They could be dissolved in stirred water with great ease and formed the typically viscous aqueous solution expected from a high molecular weight polyacrylamide product.

Example 3

An 11% w/w solution of acrylic acid monomer in liquid HFC134a containing 1% on weight of monomer of a photoinitiator, bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide, in a clear colourless polyester pressure container was deoxygenated by allowing 10% of the liquid HFC134a to evaporate via an aerosol type valve. The solution was then exposed to a broad spectrum ultra violet / visible light source for 30 minutes. The solution started to go cloudy immediately the light source was applied and after a few minutes a copious white precipitate formed. This was recovered by allowing the liquid HFC134a to evaporate. The polymer was soluble in dilute ammonia solution.

Example 4

The process of Example 3 was repeated but in addition incorporating 20,000 ppm on weight of acrylic acid of penta-erythritol tri-acrylate as a crosslinker. The polymer was recovered as in Example 3 and was water swellable in dilute ammonia solution.

Example 5

The process of Example 3 was repeated but using 1-hydroxy-cyclohexyl-phenyl-ketone as the photo initiator. Polymerisation proceeded at a slower rate to that given by the process of Example 3.

Examples 6 to 20

The process of example 3 was repeated using the monomers given in Table 1 in place of acrylic acid.

Table 1

Example	Monomer	Relative Rate	Polymer Form
6	Methacrylic acid	fast	White powder
7	DMAPMA	medium	Sticky pale yellow clumps
8	DMAPA	slow	Sticky pale yellow clumps
9	DMAEMA	slow	Sticky pale brown clumps
10	4-vinyl pyridine	slow	Sticky brown lumps
11	NVF	fast	Pale yellow powder
12	NVP	fast	Pale yellow sticky viscous material
13	HEMA	very fast	White powder going sticky in air
14	HEA	fast	White powder plus film on vessel surface
15	Methyl acrylate	medium	White powder plus film on vessel surface
16	Ethyl acrylate	medium	White powder plus film on vessel surface
17	n-Butyl acrylate	medium	White powder plus film on vessel surface
18	Methyl methacrylate	medium	White powder plus clumps
19	n-Butyl methacrylate	medium	White powder plus clumps
20	iso-Butyl methacrylate	medium	White powder plus clumps
Note: DMAPMA is dimethylaminopropylmethacrylamide; DMAPA is dimethylaminopropylacrylamide; DMAEMA is dimethylaminoethylmethacrylate; NVF is N-vinyl formamide; NVP is N-vinyl-2-pyrrolidinone; HEMA is 2-hydroxyethylmethacrylate; HEA is 2-hydroxyethylacrylate			

In each case the polymer could be recovered by evaporation of liquid HFC134a then dissolution in a suitable solvent. In some cases the polymer could be recovered as a fine powder.

Example 21

An 11% w/w solution of a monomer mixture comprising an 85:15 w/w ratio of acrylic acid: Sipomer BEM (a hydrophobically associating monomer from Rhodia) monomer in liquid HFC134A containing 300 ppm on weight of monomer of a photoinitiator bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide in a clear colourless polyester pressure container was deoxygenated by allowing 10% of the liquid HFC134A to evaporate via an aerosol type valve. The solution was then exposed to a broad spectrum ultra violet / visible light source for 30 minutes. The solution started to go cloudy immediately the light source was applied and after a few minutes a copious white precipitate formed. This was recovered by allowing the liquid HFC134A to evaporate. The polymer was soluble in dilute ammonia solution to form a viscous translucent solution.

Example 22

Example 21 was repeated but the Sipomer BEM was replaced by Sipomer SEM-25 and 400 ppm on weight of monomers of penta-erythritol tri-acrylate as a crosslinker. The polymer was recovered as a white powder which dissolved in dilute ammonia to form a viscous paste.

Claims

1. A polymerisation process comprising an initiation step, taking place between at least one initiator compound and at least one species of monomer, a propagation step and a termination step, at least the propagation step being carried out within a liquefied gas continuous phase.
2. A process according to claim 1 wherein the initiation and/or termination steps are also carried out within the liquefied gas continuous phase.
3. A process according to claim 1 or claim 2 wherein the liquefied gas continuous phase includes one or more co-solvents miscible with the liquefied gas.
4. A process according to claim 3 wherein the co-solvent is present in a proportion appropriate to form an azeotropic continuous phase.
5. A process according to claim 3 or claim 4 wherein the co-solvent is selected from other liquefied gases, straight chain-, branched- or cyclo-alkanes which are liquid at room temperature and pressure, and diethyl ether.
6. A process according to any preceding claim wherein all steps of the polymerisation process which involve the use of the liquefied gas continuous phase are carried out in a sealed pressure container.
7. A process according to claim 6 wherein the pressure container is sealed by means of an aerosol-type valve or a ball valve.
8. A process according to any preceding claim wherein the initiator compound is of the type which becomes reactive to the monomer on exposure to electromagnetic radiation.
9. A process according to any of claims 1 to 7 wherein the initiator compound is a redox couple.
10. A process according to claim 9 wherein the redox couple comprises ferrous ions and a persulphate or peroxide compound.
11. A process according to any of claims 1 to 7 wherein the initiator compound comprises an activated form of the monomer.
12. A process according to any preceding claim wherein the initiator compound is one which causes the formation of monomer free radicals.
13. A process according to any preceding claim wherein the initiator compound and the monomer are both dissolved in the liquefied gas continuous phase of the solvent.

14. A process according to any of claims 1 to 12 wherein either the initiator or the monomer is present in the liquefied gas continuous phase and the other species is present in an additional solvent phase immiscible or partially-immiscible with the liquefied gas continuous phase.
15. A process according to claim 14 wherein the additional solvent phase comprises water.
16. A process according to any preceding claim wherein a surfactant is added to the liquefied gas continuous phase.
17. A process according to claim 14 or claim 15 wherein a surfactant is added to the additional solvent phase.
18. A process according to any preceding claim wherein the termination step comprises the addition of a chain transfer or chain terminating agent.
19. A process according to claim 18 wherein the chain transfer or chain terminating agent comprises thioglycolic acid, isopropanol or nitric oxide.
20. A process according to any preceding claim wherein the termination step comprises the exhaustion of the initiator compound.
21. A process according to any preceding claim wherein the liquefied gas is selected from the group comprising C₁ to C₄ hydrofluorocarbons, C₁ to C₄ straight chain-, branched- or cyclo-alkanes selected from those which are gaseous at room temperature and pressure, C₁ to C₄ perfluorocarbons, C₁ to C₄ iodofluorocarbons, dimethyl ether, hydrogen sulphide, sulphur dioxide, chlorine, nitrous oxide, nitrogen dioxide, carbon disulphide, ammonia, carbon monoxide, carbon dioxide and argon.
22. A process according to claim 21 wherein the liquefied gas continuous phase is selected from fluoromethane, difluoromethane, trifluoromethane, pentafluoroethane, 1,1,1-trifluoroethane, 1,1,2,2-tetrafluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,1,2,3,3-hexafluoropropane, 1,1,1,2,2,3-hexafluoropropane, 1,1,1,3,3,3-hexafluoropropane, perfluoropropane, and iodotrifluoromethane.
23. A process according to claim 22 wherein the liquefied gas comprises 1,1,1,2-tetrafluoroethane.
24. A process according to any preceding claim further comprising the step of reducing the free monomer levels of the polymer by filtering and washing the polymer with liquefied gas continuous phase.

25. A process according to claim 24 wherein the filtrate and/or washings are used to form monomer-rich continuous phase for a further round of the process.
26. A process according to any preceding claim wherein at least one monomer has at least one carbon to carbon multiple bond.
27. A process according to claim 26 wherein at least one species of monomer comprises vinyl or acrylate groups.
28. A process according to claim 27 wherein the monomers comprising vinyl or acrylate groups are substituted with basic nitrogen-containing moieties or their quaternary ammonium salts.
29. The use of one or more polymers, at least one of which contains a basic nitrogen-containing moiety, as a cationic gelling agent.
30. Use according to claim 29 wherein the polymer is formed from monomers comprising those containing basic nitrogen-containing moieties and acrylate or vinyl groups or the quaternary ammonium salts thereof.
31. Use according to claim 30 wherein the polymer is formed from monomers comprising those selected from dimethylaminopropylmethacrylamide (DMAPMA), dimethylaminopropylacrylamide (DMAPA), dimethylaminoethylmethacrylate (DMAEMA), *N*-vinylformamide (NVF), *N*-vinyl-2-pyrrolidinone (NVP) and their quaternary ammonium salts.
32. Use according to any of claims 29 to 31 wherein the polymers are obtained by means of the polymerisation process of any of claims 1 to 28.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
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☒ Further documents are listed in the continuation of box C

☒ Patent family members are listed in annex

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Date of the actual completion of the International search

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INTERNATIONAL SEARCH REPORT

International Application No
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